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THE ACTIVATION OF GASES BY ADSORPTION[1]

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In his theory of the catalytic surfaces Taylor[3] suggested that the surfaces of metallic catalysts are composed of atoms in different states of lattice saturation.

In many catalytic reactions, notably those sensitive to poisons, only a part of the surface atoms produce in adsorbed molecules such changes as will facilitate a possible reaction, although almost the whole surface is capable of adsorbing gas. It seemed to be very probable that the change in adsorbed molecules is an energy-consuming activation and in the limit with diatomic molecules, a dissociation into atoms, produced by the most unsaturated surface atoms.

Several attempts were made to prove the existence of these activated molecules by studying the critical potentials of adsorbed gases.[4]

There is, however, another way of testing the presence of activated molecules on catalytic surfaces, namely, by measurements of the heat of adsorption. Although no full mathematical theory of adsorption on catalytic surfaces can be given at present, it seems to be possible to draw certain qualitative conclusions from the measured heats of adsorption on the state of adsorbed molecules, using the adsorption theory of Langmuir.

In his paper[5] Langmuir derived for a surface composed of n kinds of atoms, each adsorbing one gas molecule, an equation, which can be written in the following way:

$$\sum_1^n \frac{m_n}{N_n} = \sum_1^n \frac{b.p.\sigma_n}{1 + b.p.\sigma_n} \qquad (1)$$

where N_n is the number of surface atoms of the nth kind, m_n the number of adsorbed molecules, b a constant, p the pressure and σ_n essentially the reciprocal of the rate of evaporation of adsorbed molecules.

Assuming an equation of the Boltzmann type, σ_n will be approximately equal to $k.e^{W_n/RT}$, where W_n is the change in potential energy of a gas

by adsorption. W_n will vary according to the grade of lattice saturation of the surface atoms. Differentiation of equation 1 gives:

$$\sum_1^n \frac{dm_n}{N_n} = \sum_1^n \frac{b.\sigma_n.dp.}{(1 + b.p.\sigma_n)^2} \tag{2}$$

The differential quantities of a gas adsorbed by each kind of surface atoms will be given by the following equation, derived from equation 2:

$$\frac{\frac{dm_n}{N_n}}{\sum_1^n \frac{dm_n}{N_n}} = \frac{\frac{e^{W_n/RT}}{(1 + b.p.e^{W_n/RT})^2}}{\sum_1^n \frac{e^{W_n/RT}}{(1 + b.p.e^{W_n/RT})^2}} \tag{3}$$

It is easy to see that the first amounts of a gas at very low pressures will be preferentially adsorbed on surface atoms giving the largest W and that later the adsorption will gradually take place on the parts of the surface giving smaller W_n.

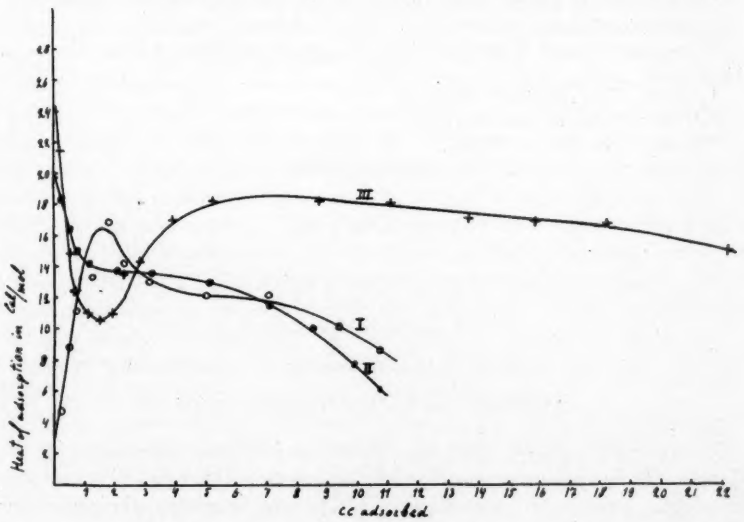
As the heat evolved by adsorption of a small quantity of gas dm on a compound surface is given by the equation:

$$Q.dm = \sum_1^n Q_n dm_n, \tag{4}$$

measurements of the differential heat of adsorption in its relation to the degree of saturation of the surface will give a picture of the surface properties, provided a certain relation can be assumed between Q_n and the corresponding W_n. In the simplest case, where no secondary process of activation of adsorbed gas is involved, Q_n will be essentially equal to W_n and the measured heat will drop from a relatively large value for the first amounts of adsorbed gas to smaller, as more gas is adsorbed on the surface. However, Fryling[6] studying the heat of adsorption of hydrogen on nickel found that (on very active nickel catalysts) the initial heat was small, increased then to a maximum and fell again. He explained his experimental results by assuming that the first portions of hydrogen were dissociated into atoms.

It seemed worthwhile to extend his measurements using a refined system. A glass vacuum calorimeter was constructed, provided with a platinum resistance thermometer and sensitive enough to measure the heat of adsorption of 0.2 cc. of hydrogen on 100 g. of a copper catalyst. All possible care was taken in eliminating the errors due to the unequal heat conductivity and other sources. In figure 1 the essential results of the measurements are represented in a summarized form, as the full series of measurements and all details will be given in another publication.[7]

Curve I is the heat of adsorption of hydrogen on an active catalyst (No. 3), curve II on a catalyst (No. 2) poisoned by a small amount of oxygen, curve III is the heat of adsorption of carbon monoxide on the active catalyst No. 3. Assuming that, as long as the adsorbed molecules are not activated, Q_n is essentially equal to W_n, but that the secondary process of activation consumes a part of the energy of adsorption W, Q_n must be equal to $W_n - w_n$, if activation takes place. If only the most unsaturated surface atoms (N_1; W_1) are able to activate hydrogen and the energy of activation w_1 is so large that $W_1 - w_1 < W_2$, the calculated curve will be similar to that found on active catalysts. Comparison of curve II with the curve (not shown) on the same sample before it was poisoned, shows that both curves are almost identical, except for the initial rise in the case



on the active catalyst, so that the curve on the poisoned sample seems to be shifted towards the ordinate axis. This means that the rôle of oxygen is to oxidize preferentially the most unsaturated surface atoms, so that the number of *activated* adsorbed molecules is decreased below the sensitivity of the apparatus, although the adsorptive capacity is only slightly changed.

The adsorptive capacity of copper for carbon monoxide is larger than for hydrogen, but, nevertheless, up to 6 cc. adsorbed, curve III is markedly symmetrical to curve I, so that the reasonable explanation of curve III will be the following: Surface atoms of two kinds (W_1 and W_2) activate carbon monoxide. Assuming $W_1 - w_1 > W_2 - w_2 < W_3$ ($W_1 > W_2 > W_3$)

we obtain a curve with all the essential features of that found experimentally.

The explanation of the calorimetric results given is in very good agreement with all previous studies on the relation between adsorptive capacity and catalytic activity and on the action of catalytic poisons. The experiments described show, however, more conclusively, that a portion of adsorbed gas is activated by the action of fields of force surrounding the unsaturated surface atoms.

I take this opportunity to express my sincere thanks to Professor H. S. Taylor for his suggestion of the present work and to the International Education Board for the Fellowship, which enabled me to carry on this investigation.

[1] Contribution from the Laboratory of Physical Chemistry, Princeton University.

[2] International Research Fellow.

[3] The fourth Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, 30, 145 (1926).

[4] *J. Phys. Chem.*, 30, 1356 (1926).

[5] *J. Amer. Chem. Soc.*, 40, 1361 (1918).

[6] *J. Phys. Chem.* 30, 818 (1926).

[7] *Zeitsch. phys. Chemie.*, forthcoming publication.

LUMINESCENCE DUE TO RADIOACTIVITY

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It is generally known that all radioactive substances luminesce in the dark. The luminescence is excited by the passage through the substances of alpha-, beta- and gamma-rays, which are characteristic radiations of various radioactive elements. The luminescence produced by these rays is very different in nature than the rays themselves. Alpha-, beta- and gamma-rays are atomic in nature, subject entirely to the atomic forces which are beyond our control. They represent spontaneous emissions of atomic energy. The luminescence produced by them is molecular in nature. It is the result of changes in molecular energy and, therefore, is largely affected by the physical and chemical changes in the substance.

Luminescence produced by radioactivity has been the subject of numerous researches. A number of theories have been advanced to explain its nature. It has been suggested, for example, that the luminescence may be due to ionization in the substance, the recombination of the ions giving out the light. This would be similar to a discharge in rarefied gases. If this

were true a luminescent substance would glow with a uniform intensity as long as the exciting source remained constant. It has been shown by E. Marsden[1] that this is not the case. Luminescent zinc-sulphide, which was studied by this author, showed a decided decay in time after allowing for the decay of exciting source. To explain this fact Rutherford[2] suggested that the luminescence may be due to the existence in the material of a finite number of molecular aggregates which he calls active centers. The passage of alpha-rays through one or more active centers would destroy them, giving out a flash of light. According to this theory an active center once destroyed cannot be regenerated. This would result in the substance decaying in time according to an exponential curve approaching zero luminosity as a limit.

Patterson, Walsh and Higgins[3] investigating the decay of luminosity in the same substance showed that this theory does not agree with their observations except at initial stages of luminescence. When the time is prolonged the luminosity does not approach zero as was required by this hypothesis but tends to reach a constant value and remain so for an indefinite period of time. To explain this phenomenon they suggested the existence of two factors in the luminescent substance; one, a decay according to an exponential law, and the second a regeneration also according to an exponential. The combination of two such curves with proper constants seemed to explain completely the facts observed by them on this material. J. A. Rodman[4] investigating the decay of luminescence in pure radium bromide showed that the decay of luminescence of this substance cannot be explained by this theory. Also L. E. Smith[5] investigating the luminescence of pure barium bromide obtained results which cannot be explained by either one of these theories.

It can be shown that three distinct types of luminescence due to radioactivity exist in these materials. These three usually exist together in a given material with varying degrees of intensity, resulting in a very complex curve to represent the rise and the decay of luminescence in the substance. The first type is represented by the well-known substance synthetic zinc sulphide under the action of alpha-rays, after this has reached a state of equilibrium. The energy is supplied by the exciting rays themselves. If active centers exist they are formed as well as destroyed by the passage of the alpha-rays through the substance. The process then is what is known as a reversible process where the rays are capable of forming, as well as destroying the molecular modification in the compound.

Experimental evidence of the ability of alpha-rays to create such active centers in another substance was brought out by the research of L. E. Smith. His time-luminosity curves of pure barium bromide show an increased luminosity for a period of ten hours under the action of alpha-rays. If a similar reaction takes place in zinc sulphide, which is quite probable,

the steady luminescence of this material is completely explained. Therefore, we can say that in zinc sulphide which has reached a steady state, the action of the alpha-rays is predominantly of this reversible type.

The second type can be best represented by the luminescence of pure radium or barium bromide. Barium bromide is not luminescent under the action of alpha-rays until it has been given a heat treatment. When it is heated to a temperature of 550°C. and quickly cooled it acquires the property of luminescing under the action of alpha-rays. It is quite evident that the energy emitted as luminescence is absorbed by the substance during the process of heating. The molecular agitations at higher temperature seem to result in configurations with a higher quantum state. These configurations are fairly stable if undisturbed. The passage of alpha-rays destroy these configurations giving out the light. This results in a decay of luminosity in time. The luminosity, however, can be completely regenerated if the substance is allowed to absorb another supply of energy by raising it to a high temperature and then cooling. The dependence of luminosity on the temperature of the heat treatment was brought out both by Karrer, Kabakjian[6] and by L. E. Smith.

The third type of luminescence is that represented by a fluorite crystal and is generally known as thermo-luminescence. The energy in this case is furnished by alpha-, beta- and gamma-rays and liberated by molecular agitation in the crystal. If a calcite crystal is brought near a beta-ray source it shows a very faint luminosity. As the time of exposure increases the luminosity of the crystal also rises until a steady state is reached. The amount of energy that can be absorbed by such a crystal is a function of the temperature of the crystal. The lower the temperature, the greater the energy absorbed. The molecular configurations of higher quantum state are more stable at lower temperatures. If such a crystal is exposed to beta-rays at a temperature of liquid air it can absorb large quantities of energy which will be released as luminescence when the temperature of the crystal is raised by taking it out of liquid air. Placing the crystal on a hot plate will greatly intensify the luminescence. It can be shown that the release of this luminous energy takes place, in case of certain fluorites in several distinct stages with maxima in varying wave-lengths.

It is generally assumed that luminescence of these types is due to presence of minute quantities of impurities in the various substances. This is true in many cases. Researches in this laboratory have shown that this is not universally true. A number of pure compounds have been shown to luminesce under the action of alpha-, beta- and gamma-rays.

Recapitulation.—It can be said that three different types of luminescence due to radio-activity can be distinguished. In most substances all three exist at the same time with varying degrees of intensity, resulting in very complex curves representing the rise and decay of luminescence.

This probably accounts for the failure of any one theory to explain all the observations on different compounds. Even though it may not be possible to completely separate these in any one compound it is possible to select such compounds where one or the other type largely predominates and by a study of these it may be possible to formulate a general theory of luminescence due to radioactivity.

[1] E. Marsden, *Proc. Roy. Soc.*, **83A**, p. 548 (1909–10).
[2] E. Rutherford, *Ibid.*, **83A**, p. 561 (1909–10).
[3] Patterson, Walsh and Higgins, *Proc. Phys. Soc. London*, **29**, p. 215 (1917).
[4] J. A. Rodman, *Physic. Rev.*, **23**, p. 478 (1924).
[5] L. E. Smith, *Ibid.*, **28**, p. 431 (1926).
[6] E. Karrer and D. H. Kabakjian, *J. Frank. Inst.*, **186**, p. 317 (1918).

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*RADIATION AND ABSORPTION ON SCHRÖDINGER'S THEORY**

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Radiation and absorption of light by atoms can be treated by replacing the atoms by a set of oscillators, whose natural frequencies are the frequencies of quantum transitions, as has been shown by the writer in a previous paper.[1] By means of Schrödinger's wave mechanics,[2] it is possible to place the theory on a more satisfactory foundation than was possible before, at the same time changing the physical ideas to some extent. Schrödinger has made a beginning in this direction, but it is the purpose of the present note to sketch a more detailed treatment of radiation and absorption.

The fundamental feature of Schrödinger's method is that there is a function ψ of space and time, such that the product of ψ and its conjugate, $\psi\bar{\psi}$, gives the relative volume density of electricity, the total density being $e\psi\bar{\psi}$ (at least, when the atom contains only one electron; see Schrödinger, *Ann. d. Phys.*, **81**, p. 118). The function ψ can be written, as Schrödinger shows, $\psi = \Sigma(n)c_n \exp(2\pi i E_n t/h)u_n$, where exp represents e raised to that power, E_n is the energy of the nth quantum state, u_n is a function of the space coördinates alone (assumed to be real), and c_n is an arbitrary constant (which may be complex). Then we have $\psi\bar{\psi} = \Sigma(nm)c_n\bar{c}_m \exp(2\pi i(E_n - E_m)t/h)u_n u_m$. The terms with indices n, m represent an amount of charge oscillating with the frequency $(E_n - E_m)/h$, and are to be identified with the oscillator connected with this transition frequency of the atom. The electric moment of this oscillator is then e multiplied by the average value of the vector $r(x, y, z)$ averaged over the charge; that

is, letting $e\int r\ u_n u_m dv = p_{nm}$ (a vector), it is $(c_n\bar{c}_m \exp(2\pi i(E_n - E_m)t/h) + \bar{c}_n c_m \exp(-2\pi i(E_n - E_m)t/h))p_{nm}$. The quantities p_{nm} are shown by Schrödinger to constitute Heisenberg's matrix for the electric moment. The amplitude of the oscillator then depends both on the c's and p's. The essentially new feature in Schrödinger's analysis, not found in Born and Heisenberg's matrices, is the presence of the arbitrary constants c_n. Although these are constant when no external forces act on the atom, they vary slowly with time under the action of radiation, and this variation represents the way in which the distribution among the various stationary states changed with time. Following Born,[3] we identify $c_n\bar{c}_n$ with the fraction of atoms in the nth state, giving up all definite connection between individual atoms and individual oscillators. Then the time variation of $c_n\bar{c}_n$ gives the rate of change of the number of atoms in the nth state. We shall find that the secular variation of $c_n\bar{c}_n$ is given by

$$\frac{d}{dt}(c_n\bar{c}_n) = \sum_{E_m > E_n}(m)c_m\bar{c}_m(A_{mn} + B_{mn}\rho(\nu_{mn})) + \sum_{E_m < E_n}(m)c_m\bar{c}_m B_{mn}\rho(\nu_{mn}) - c_n\bar{c}_n\Big\{\sum_{E_m > E_n}(m)B_{nm}\rho(\nu_{nm}) + \sum_{E_m < E_n}(m)\ (A_{nm} + B_{nm}\rho(\nu_{nm}))\Big\}, \quad (1)$$

where A_{mn} and B_{mn} are the Einstein coefficients of probability of spontaneous and forced transition, and $\rho(\nu_{nm})$ is the energy density in the external field at the frequency ν_{nm} of a quantum transition. On Born's interpretation of the c's, these equations represent the ordinary Einstein equations of probability of radiation and absorption. The first term represents the increase of atoms in the nth state on account of spontaneous and forced radiation from all higher levels, the second the forced absorption from all lower levels; the third and fourth similarly represent the decrease of atoms in the nth state on account of forced absorption to higher levels, and of spontaneous and forced emission to lower levels. The next sections contain the derivation of the equation (1).

Derivation of Perturbation Equations.—To find the time variation of the c's, we adopt a method somewhat more direct than Schrödinger's, which will be merely sketched here. We seek a solution of Schrödinger's equation $\Delta\psi - (8\pi^2/h^2)V\psi - (4\pi i/h)\dot{\psi} = 0$, where $V = V_0 + \lambda V_1$, of the form $\sum(n)c_n \exp(2\pi i E_n t/h)u_n$, where E_n and u_n have the same values as in the unperturbed case, but where $c_n = c_n^0 + \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + \ldots$, c_n^0 being independent of time, but the other c's being, in general, functions of time. Then it is easy to show that

$$c_n^{(k)} = (2\pi i/h)\sum(m)\int_{t_0}^{t} c_m^{(k-1)} \exp(2\pi i(E_m - E_n)t/h)\ (V_1)_{nm}dt \quad (2)$$

where $(V_1)_{nm}$ is the component of the matrix of V_1, and t_0 is the instant

at which the motion has its unperturbed value. From this equation we can obtain all the c's by quadrature.

Application to External Radiation Fields.—We assume the perturbative potential to be $-\lambda(p\cdot E)$, where p is the electric moment, E the external electric field, which is assumed to be given by a Fourier series $E = \sum(k)a_k \exp(2\pi i\nu_k t)$, where the a_k's are vectors, and where in order to have E real we have $a_{-k} = \bar{a}_k$. Then we have $(V_1)_{nm} = -\sum(k)(a_k\cdot p_{nm}) \exp(2\pi i\nu_k t)$. This gives, using equation (2),

$$c_n^{(1)} = -\sum (mk)\, c_m^0 (a_k\cdot p_{nm}) \frac{\exp(2\pi i(h\nu_k + E_m - E_n)t/h) - \exp(2\pi i(h\nu_k + E_m - E_n)t_0/h)}{h\nu_k + E_m - E_n},$$

agreeing with Schrödinger. We must, however, compute the second approximation:

$$c_n^{(2)} = \sum (m\ k\ m'k') c_m^0 \frac{(a_k\cdot p_{mm'})(a_{k'}\cdot p_{m'n})}{h\nu_k + E_m - E_{m'}} \exp(2\pi i(h\nu_k + h\nu_{k'} + E_m - E_n)t_0/h)$$
$$\left\{ \frac{\exp(2\pi i(h\nu_k + h\nu_{k'} + E_m - E_n)(t-t_0)/h) - 1}{h\nu_k + h\nu_{k'} + E_m - E_n} - \frac{\exp(2\pi i(h\nu_{k'} + E_{m'} - E_n)(t-t_0)/h) - 1}{h\nu_{k'} + E_{m'} - E_n} \right\}$$

We are now in position to compute $c_n\bar{c}_n$. This is $c_n\bar{c}_n = c_n^0\bar{c}_n^0 + \lambda(c_n^0\bar{c}_n^{(1)} + c_n^{(1)}\bar{c}_n^0) + \lambda^2(c_n^0\bar{c}_n^{(2)} + c_n^{(1)}\bar{c}_n^{(1)} + c_n^{(2)}\bar{c}_n^0) + \ldots$.

The terms in λ are proportional to the first power of the a_k's. But as usual, in treating radiation problems, we must average over all possible phases of the external field, and in doing this these terms average to zero. Thus we have left only the terms in λ^2. Further, in this term we have products of the a_k's of different external frequencies, and we know that all those vanish in the averaging except the ones for which we have the product of a particular component of an amplitude with its conjugate as $(a_k)_x(a_{-k})_x$. In a radiation field we can make connection between the average value of these products and the energy density, each equaling $(2\pi/3)\rho(\nu_k)d\nu_k$, where we must at the same time replace the summation over k by an integration with respect to ν_k. If we assume $\rho(\nu_k)$ to be approximately constant over each absorption line, we may take it outside the integrals. The terms have large values when simultaneously the two frequencies in the denominator are nearly zero. We neglect all terms in the summation for which this is not true, leaving as the important terms, after some reduction,

$$c_n^0\bar{c}_n^{(2)} + c_n^2\bar{c}_n^0 = -\frac{4\pi}{3}c_n^0\bar{c}_n^0\sum(m')(p_{nm'}\cdot p_{m'n})\rho(\nu_{m'n})$$
$$\int\frac{1-\cos(2\pi(h\nu_k+E_n-E_{m'})(t-t_0)/h)d\nu_k}{(h\nu_k+E_n-E_{m'})^2}$$
$$= -\frac{8\pi^3}{3h^2}(t-t_0)c_n^0\bar{c}_n^0\sum(m')(p_{nm'}\cdot p_{m'n})\rho(\nu_{m'n}).$$

Similarly,

$$c_n^{(1)}\bar{c}_n^{(1)} = \frac{8\pi^3}{3h^2}(t-t_0)\sum(m)(c_m^0\bar{c}_m^0)(p_{nm}\cdot p_{mn})\rho(\nu_{nm}).$$

But $(p_{nm}\cdot p_{mn}) = e^2D_{nm}^2/4$, where D_{nm} is the amplitude associated with the oscillator (nm); and in terms of this we have $B_{nm} = 2\pi^3e^2D_{nm}^2/3h^2 = 8\pi^3(p_{nm}\cdot p_{mn})/3h^2$. Thus, putting $\lambda = 1$, $c_n\bar{c}_n = c_n^0\bar{c}_n^0 + (t-t_0)\sum(m)(c_m^0\bar{c}_m^0 - c_n^0\bar{c}_n^0)B_{nm}\rho(\nu_{nm})$, and the time rate of change is exactly the part of equation (1) arising from external radiation.

Spontaneous Radiation.—Spontaneous radiation cannot be treated as satisfactorily as absorption in the present state of the theory. The most obvious way to accommodate the radiation resistance, which by classical analogy we suppose to be $2\dddot{p}/3c^3$, would be to put in a perturbative potential $V_1 = -(2(p.\dddot{p})/3c,^3$ with matrix $(V_1)_{mn} = -(2/3c^3)\sum(k)(p_{mk}\cdot p_{kn})(2\pi i(E_k-E_n)/h)^3$. But this is not successful; the resulting solution is one for which $\sum(n)c_n\bar{c}_n$ does not remain constant with time. That is to say, if the solution were correct, the total number of atoms would change with time, which shows that there is some flaw in the method. This does not conflict with Schrödinger's proof that $\int\psi\bar{\psi}dv = \sum(n)c_n\bar{c}_n$ is constant in time; for, on examination of this proof, it will be found that it does not hold in general if the perturbative potential is imaginary, as it obviously is here. We infer that Schrödinger's equation does not apply in its present form to such a case. This is only natural; we are dealing with a non-conservative force, in which the energy does not stay constant, and such systems cannot be treated by the Hamiltonian method on ordinary mechanics. There is no reason then to suppose that they could be treated by Schrödinger's method, which is analogous to the Hamiltonian.

The next method which suggests itself is that of treating the radiation resistance as an external force varying with the time, with the frequencies of motion of the oscillators and properly adjusted phase. This method has been followed with success in discussing radiation in the classical case.[4] But another difficulty appears which can be best illustrated by a simple example. Suppose we have a perturbative potential λp^2, so that $(V_1)_{nm} = \sum(k)p_{nk}\cdot p_{km}$. Then, neglecting the term in t_0, we have $c_n = c_n^0 + \lambda\sum(ml)c_m^0(p_{ml}\cdot p_{ln})\dfrac{\exp(2\pi i(E_m-E_n)t/h)}{E_m-E_n}$. The secular terms, in which

we are particularly interested, come from setting $E_m = E_n$, and are $c_n = c_n^0 + c_n^0(2\pi i/h)t\lambda \sum (l)p_{nl}\cdot p_{ln}$. On the other hand, suppose we tried to replace the potential by the product of λp, and a function of time equivalent to p; that is, $\sum (nm)c_n^{0-}c_m^0 \exp(2\pi i(E_n - E_m)t/h)p_{nm}$. Then we have, by the previous method,

$$c_n = c_n^0 + \lambda \sum (mkl)c_m^0 c_k^{0-}c_l^0(p_{nm}\cdot p_{kl})\frac{\exp(2\pi i(E_m - E_n + E_k - E_l)t/h)}{E_m - E_n + E_k - E_l}.$$

The secular terms, coming by setting the denominator equal to zero, are $c_n = c_n^0 + c_n^0(2\pi i/h)t\lambda \sum (l)c_l^{0-}c_l^0(p_{nl}\cdot p_{ln})$. The periodic terms, of course, differ entirely from the correct ones, involving sums of quantum frequencies which are not themselves quantum frequencies. But even the secular term is wrong; each term of the summation over l contains the factor $c_l^{0-}c_l^0$, which should not appear. Of course, it is obvious that, if we put in a potential of the second power in the c's, instead of one independent of the c's, the result will have a superfluous factor in squares of c's. To get the right answer for the secular terms, it is easy to see that our external function of time must be

$$\sum (nm)\frac{c_n^0 c_m^0}{c_m^{0-}c_m^0}p_{nm}\exp(2\pi i(E_n - E_m)t/h).$$

By analogy, we should naturally suppose that the external function of time to be substituted for the radiation resistance $2p'''/3c^3$ was

$$\sum (nm)\frac{c_n^{0-}c_m^0}{c_m^{0-}c_m^0}\frac{2}{3c^3}(2\pi i(E_n - E_m)/h)^3 p_{nm}\exp(2\pi i(E_n - E_m)t/h).$$

But we readily find by trying this that it gives $\sum (n)c_n\dot{c}_n$ varying with time. A slight variation, however, removes this difficulty: we let the function be

$$\sum_{E_n > E_m}(nm)\frac{c_n^{0-}c_m^0}{c_m^{0-}c_m^0}\frac{2}{3c^3}(2\pi i(E_n - E_m)/h)^3 p_{nm}\exp(2\pi i(E_n - E_m)t/h).$$

$$+\sum_{E_n < E_m}(nm)\frac{c_n^{0-}c_m^0}{c_n^{0-}c_n^0}\frac{2}{3c^3}(2\pi i(E_n - E_m)/h)^3 p_{nm}\exp(2\pi i(E_n - E_m)t/h).$$

Using this as an external force, we have

$$c_n = c_n^0 - \lambda\sum_{E_k > E_e}(mkl)\frac{c_m^0 c_k^0}{c_e^0}\frac{2}{3c^3}(2\pi i(E_k - E_e)/h)^3(p_{ke}\cdot p_{nm})$$

$$\frac{\exp(2\pi i(E_m - E_n + E_k - E_e)t/h) - \exp(2\pi i(E_m - E_n + E_k - E_e)t_0/h)}{E_m - E_n + E_k - E_e}$$

$$-\lambda\sum_{E_k < E_e}(mkl)\frac{c_m^{0-}c_e^0}{c_k^{0-}}\frac{2}{3c^3}(2\pi i(E_k - E_e)/h)^3(p_{ke}\cdot p_{nm})$$

$$\frac{\exp\,(2\pi i(E_m - E_n + E_k - E_e)t/h) - \exp\,(2\pi i(E_m - E_n + E_k - E_e)t_0/h)}{E_m - E_n + E_k - E_e}.$$

The secular terms are for $E_m = E_l$, $E_n = E_k$. Thus the first summation reduces to a summation over m, for terms for which $E_m < E_n$, and the second over those for which $E_m > E_n$. Then

$$c_n = c_n^0 - (2\pi i/h)(t - t_0)\lambda \sum_{E_m<E_n} (m) c_n^0 \frac{2}{3c^3} (2\pi i(E_n - E_m)/h)^3 (p_{nm} \cdot p_{nm})$$

$$- (2\pi i/h)(t - t_0)\lambda \sum_{E_m>E_n} (m) \frac{c_m^0 \bar{c}_m^0}{\bar{c}_n^0} \frac{2}{3c^3} (2\pi i(E_n - E_m)/h)^3 (p_{nm} \cdot p_{nm}).$$

From this, introducing Einstein's coefficient A_{nm}, we have

$$\frac{d}{dt}(c_n \bar{c}_n) = -\sum_{E_m<E_n} (m) c_n \bar{c}_n A_{nm} + \sum_{E_m>E_n} (m) c_m \bar{c}_m A_{nm}$$

which is the part of the equation (1) coming from spontaneous radiation. It is readily verified that, to the order to which we are working, the perturbations of the two sorts merely add, without cross terms.

* NOTE ADDED IN PROOF: Dirac (*Proc. Roy. Soc.*, **112**, p. 661, 1926), in a paper which the writer had not seen when the present note was sent in, treats absorption by a similar method. Since he does not discuss radiation, and since the present discussion of absorption is somewhat fuller than his, it seemed better not to withdraw the present paper.

[1] J. C. Slater, *Physic. Rev.*, **25**, p. 395, 1925.
[2] E. Schrödinger, *Ann. Physik*, **79**, p. 361, 489, 734; **80**, p. 437; **81**, p. 109, 1926.
[3] M. Born, *Zeits. Physik*, **38**, p. 803, 1926.
[4] J. H. Van Vleck, *Physic. Rev.*, **24**, p. 347, 1924.

THE DEATH RATE FROM DIPHTHERIA IN MASSACHUSETTS FOR 51 YEARS, 1875–1925

BY CARL R. DOERING

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Read before the Academy November 9, 1926

Between 1842, the first year in which figures at all comparable to subsequent ones are available, and 1876 the death rate from diphtheria in Massachusetts pursued an erratic course in great waves from about 40 (per hundred thousand population) to nearly 200, but since 1876 has fallen steadily with only such fluctuations as might be expected and with no tendency to increase.

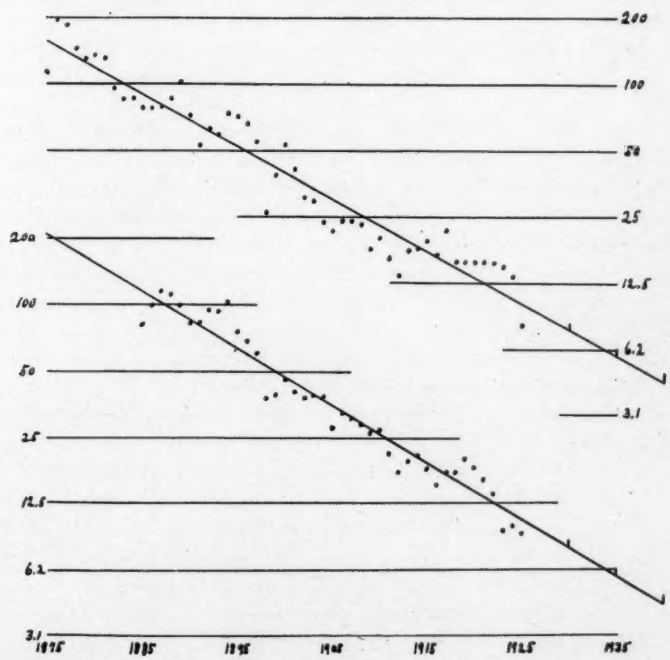
The death rates for Massachusetts for 1875 to 1925 are plotted on semi-

logarithmic paper in the figure, and under them, with a separate scale those for New York State from 1885 to 1925. The graph shows the following facts:

(*a*) The rates have been nearly equal in Massachusetts and in New York.

(*b*) The rates of decline of the rates in the two states have been the same and equal to about $5^1/_2\%$ per annum.

(*c*) The rates of decline in Massachusetts in the three 17-year periods 1875–1891, 1892–1908, 1909–1925 and in New York for the last two



periods have not differed from the general rate by more than might be expected in a disease so irregular as diphtheria.

(*d*) The percentage variability of the rates, represented approximately by departures on a logarithmic scale, has been about the same throughout the five 17-year periods.

(*e*) There is a marked correlation in the two states between the departures of the rates from their trends.

The numerical calculations verify the graphical interpretations. (*b*) Rate of decline for Massachusetts, expressed in logarithms, $-0.024 \pm$

0.001; for New York -0.027 ± 0.001. (*c*) Rates of decline for 17-year periods in Massachusetts, -0.025 ± 0.0045, -0.035 ± 0.0045, -0.13 ± 0.0045; for New York, -0.035 ± 0.004, -0.024 ± 0.004. The scattering of these from their mean -0.026 is about twice as great as their standard deviations would indicate and might be barely significant, e.g., the highest rates of decline -0.035 occur in the period 1892–1908 in which the use of antitoxin and bacteriological diagnosis was introduced and spread, but the inference is statistically dubious. (*d*) In Massachusetts in the three 17-year periods, the mean logarithmic departures (without regard to sign) from the general trend are 0.066, 0.086, 0.082 and in New York 0.060, 0.060. (*e*) The coefficient of correlation of the logarithmic deviations in Massachusetts and New York for 41 years 1885–1925 is 0.57 ± 0.10, which implies a large degree of common causation in the annual fluctuations in the two states.

Such a description shows what has happened in respect to the death rate in the very complicated symbiosis of the pathogenic organism and the human population; it does not allocate or even indicate specific causes. The whole phenomenon is a summation of numerous changing factors some of which tend to cause an increase of deaths from the disease and others a decrease, e.g., (*a*) quarantine and isolation, (*b*) methods of diagnosis, (*c*) changes in reported classifications, (*d*) types and virulence of the disease,[1] (*e*) natural immunity of the population, (*f*) use of antitoxin since 1894, (*g*) recent introduction of artificial immunization, (*h*) increasing urbanization, (*i*) immigration, (*j*) increased standard of living, (*k*) increase in general hygiene, etc. Studies on the effects of some of these variables are in progress.

In the absence of any determination of the relative importance of various causes in determining the continued decrease of the diphtheria death rate, and of estimates of the future effectiveness of those causes toward a further reduction of the rate, prophesy cannot be made. This may be said: If the trend continues for the next fifteen years at its past rate, we should expect, except for statistical fluctuations, rates of 7.6 by 1930, of 5.8 by 1935, and of 4.4 by 1940. It is to be hoped that the wider use of curative and preventive measures already known and yet to be discovered may markedly improve the picture.

[1] Theobald Smith, "Some Problems in the Life History of Pathogenic Microörganisms," *Amer. Medicine*, **8**, No. 17, Oct., 1904. Charles V. Chapin, Sedgwick Lecture, 1926 (not yet published). These eminent authorities are of the opinion that pathogenic parasities in the course of their natural evolution tend to become less virulent in effect upon their hosts and that the hosts tend to become more immune to the effects of the parasites.

A FUNDAMENTAL THEOREM IN MODIFIABILITY

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Communicated November 22, 1926

Let S represent any situation, such as the sound of a word, and let R_1, R_2, R_3, etc., represent any responses which a man makes to that situation. Denote by C_1, C_2, C_3, etc., the connections in the mind or brain whereby S evokes or is followed by R_1, R_2, R_3, etc. C_1, C_2 and C_3 may be considered, more abstractly, as merely the probabilities that $S \longrightarrow R_1$, $S \longrightarrow R_2$, $S \longrightarrow R_3$, etc., will happen if S happens. Let f_1, f_2, f_3, etc., represent the frequencies of occurrence of C_1, C_2, C_3, etc. (that is, of $S \longrightarrow R_1$, $S \longrightarrow R_2$, $S \longrightarrow R_3$, etc.), up to a time, t, and let their frequencies be very unequal. Suppose that, after that time, the situation S occurs n times. Will the more frequent connections increase in frequency at the expense of the less frequent? For example, if the syllable jeb was connected with 1 eight times, with 2 once, and with 3 once, and if jeb then is presented a hundred or so times more, will it in the end tend to evoke 1 more then eight times out of ten, and to evoke 2 and 3 less than once out of ten?

Psychologists, insofar as they have faced this question at all, have usually taken it for granted that the first answer is correct, but no proof of its correctness has ever been given.

The theoretical importance of the question lies in its bearing upon the laws of use and effect and upon certain theories of facilitation and inhibition in the nervous system. The law of use asserts that, other things being equal, the more frequently S connects with or evokes any given R, the stronger becomes the tendency for it to do so in the future. If, for example, by some means R_2 is somehow made to follow closely upon S a hundred times, the tendency for S to evoke R_2 will become stronger than it was, and may become stronger than some other tendency, $S \longrightarrow R_1$, which was originally stronger than it. This law has been generally accepted as a part of orthodox psychology.

The law of effect asserts that what happens as an effect or consequence or accompaniment or close sequel of a connection works back upon the connection to strengthen or weaken it. This law has not been so generally accepted.

If the first answer is true, the law of use has wide influence, though the law of effect may also be true. If the second answer is true, the law of use has a restricted influence, and some law of effect *must* be true. Also, if the quantitative increase in the strength of a more frequent response by its greater relative frequency, is very small, there is a similar, though not so extreme, magnification of the importance of the law of effect.

If the first answer is correct, there must be some physiological selection by repetition. It may be a change at the synapses, whereby the repeated conduction of a stimulus over the same path actively enriches the tendency so to conduct at the expense of tendencies to conduct elsewhere. Or it may be some sort of selective integration, whereby the repeated action of more or less of the associative system as a whole in a certain pattern depresses the tendency for it to act in other patterns. Or it may be something else. But if an animal which responds to S by R_1 90 times and by R_2 10 times, by this mere fact of relative frequency, becomes an animal which responds to S by R_1 91 times and by R_2 9 times, and so on, until it is an animal which responds to S by R_1 100 times and by R_2 0 times, there has been some active influence of the physiological basis of $S \longrightarrow R_1$ upon the physiological basis of $S \longrightarrow R_2$, increasing the probability of the former occurrence at the expense of the probability of the latter.

On the other hand, if the first answer is false, or if the quantitative amount of influence of relative frequency upon future relative frequency in favor of the more frequent is small, we must be suspicious of "drainage" theories and the like, in general. The case of repetition strengthening the strong at the expense of the weak is a favored case for them.

The importance of the question and answer for the practical control of learning will be only briefly mentioned here. In proportion as repetition *per se* increases the strength of the more frequent connection at the expense of the strength of the less frequent, mere practice may be trusted to produce learning as soon as the desired connection is put at a level of strength above any other one connection, provided that other things (such as intensity, recency, or the effects of the connections) do not act against it in sufficient strength. In proportion as repetition *per se* simply confirms the *status quo*, mere practice will often be fruitless, and attention should be given to avoiding practice in error from the outset, and to making the effects of the connections such as will strengthen the desired one and weaken the others.

We have carried out an extensive and varied series of experiments, the results of which all seem to show that the negative is the true answer—that the mere repetition of S, no matter how many times, does not strengthen the stronger C's at the expense of the weaker. These experiments will be described fully and the quantitative results presented in detail in a special monograph. We shall give here only statements of their general nature and outcome.

In experiments I to IV S is a strip of a given length, and R_1, R_2, R_3, etc., are estimates of the length. The initial frequencies (that is the frequencies up to time t) of C_1, C_2, C_3, etc., vary from one out of thirty to from four to ten out of thirty. More estimates of S are then made, the last thirty of which are used for comparison with the first thirty. Twenty-

five different S's were used, each one with six different individuals. If we uniformly denote the initially most frequent response by R_1, and its frequency in the first 30 by f_1 and its frequency in the last 30 by F_1, F_1 does not on the whole exceed f_1.

In experiments V to XX, S is the signal "Draw a two-inch line" or "draw a three-inch line" or the like, given to a person whose eyes are kept closed so that he never sees any line that he draws. The responses are classified as R_1, R_2, R_3, etc., according to their length. f_1, f_2, f_3, etc., are determined from the first hundred or more occurrences, or from the occurrences in the first day or two of the experiment. The total number of repetitions of S varies from 750 to over 5000. We have records from eleven individuals, most of whom used four different lengths. Letting f_1 be the percentile frequency of the response of greatest initial frequency and F_1 be the percentile frequency of that response at the end of the experiment, we find again no increase of F_1 over f_1.

Experiments XXI and XXII were of the same general plan as experiments V to XX. Angles were drawn instead of lengths. F_1 again shows no increase over f_1.

In experiment XXIV,[1] S was a word heard. R_1, R_2, R_3, etc., were the numbers 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9. The subjects of the experiment were required to respond by writing some one of these numbers, whichever one came to mind when the word was heard. A total of 3840 words were heard, including 60 occurrences of *admire*, 60 occurences of *bread* and 40 occurrences each of *able*, *answer*, *beast*, *cannot* and six other words. These 520 occurrences were scattered throughout the 3840. Six individuals performed the experiment, hearing 320 words daily for twelve week-days.

We find R_1 for the first twenty occurrences of each of the twelve words, as before; and find the gain in frequency of it in later successive tens. Taking all the 72 cases together, the initially most frequent response loses as often as it gains.

In experiment XXVI[2] S was a sound (for example, *aw* as in saw), and R_1, R_2, R_3, etc., were various ways of spelling it. The sounds *a* as in late, *ee* as in week, *ow* as in how, *aw* as in saw, *o* as in so, *s* as in so and *c* as in cow, were given from 210 to 294 times, in 480 nonsense words like kaseédawb and rośanowr. Six subjects spelled these words. We find for each sound for each person the most frequent response in the first thirty occurrences and then observe what frequency it has in the last thirty. The *f* sound occurred 124 times in all, and for it we use the first and last twenty. The sum of the f_1's is 899 out of a total frequency of 1480; that of the F_1's is 919 out of 1480. There is thus a gain of only two per cent.

The case of responding to a sound by a spelling is a favored case for mere repetition. The initially most frequent response has, on the average,

a much greater frequency than all of its competitors put together have, and there are, in most cases, 246 or more repetitions. Yet persons retained the rare R_2's, R_3's, etc., at the end almost as at the beginning.

From these and other experiments we conclude that mere frequency of use of $S \longrightarrow R_1$ does not strengthen it at the expense of weaker connections $S \longrightarrow R_2$, $S \longrightarrow R_3$, etc. Greater relative frequency is not a selective force. To explain the facts of modifiability some influence from the consequences of a connection is required. Facilitation and inhibition among the different connections from a situation are not explainable by "drainage" toward the stronger, and all physiological and psychological theories which involve similar forms of drainage are under suspicion.

[1] Experiment XXIII, not reported here, was like experiment XXIV in general nature and result.

[2] Experiment XXV was like experiment XXVI, but shorter, and undertaken by many more persons. It showed no gain of the strong at the expense of the weak.

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*A SUMMARY OF SOME OF THE RESULTS FROM AN EXPERIMENTAL STUDY OF THE EAST KENTUCKY MOUNTAINEERS.**

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Communicated December 17, 1926

1. The East Kentucky Mountaineers are mainly the descendants of Scotch-Irish ancestry, with some English and German heredity and a small amount of French Huguenot blood. After the Revolutionary War the eastern seaboard states, becoming thickly settled, occasioned movements of great numbers of families westward. Settlers came to the Kentucky Mountains from Central Pennsylvania, from Virginia, from North and South Carolina and a few from Maryland. The mountain people of today are a blend from the mingling of these several strains.

A selection of subjects to fairly represent these people was no mean task. In the first place the question of counties arose. The mountainous area of Kentucky occupies at least 30 counties. Three counties were selected. Two of these counties were chosen because they were still isolated, practically without railroads (two miles of road in one county, and eight in the second) but at the same time, through Settlement and Community schools, founded by outsiders, they had excellent educational facilities in some sections. The third county was selected for one of these reasons:

an excellent school run by outsiders, but in another respect it differed from the two other counties, for during the last ten years coal mines and lumber camps have opened up the greater part of the country. The possibility of contrasting I. Q. averages was believed to be excellent between this county and the two others.

2. Intelligence Tests were given to 1945 subjects. Their ages ranged from 5 to 23; their grades ranged from the 1st through the 12th grade. Some of the results, expressed in terms of I. Qs., follow:

TABLE 1

INTELLIGENCE QUOTIENT AVERAGES BY CHRONOLOGICAL AGES

AGE GROUP	NUMBER OF CASES	I. Q. AVERAGE	STANDARD DEVIATION
5 and 6 year group	88	86.6[a]	20.2
7 year group	113	85.1[b]	16.0
8 year group	180	81.0	12.1
9 year group	179	79.2	13.8
10 year group	190	78.6	14.8
11 year group	191	77.2	14.8
12 year group	211	75.4	17.7
13 year group	177	73.1	13.3
14 year group	174	74.6	16.0
15 year upward group	442	81.1	16.7
Totals	1945	79.0	

[a] Very highly selected group—almost all of these 88 subjects were located in four Community schools.

[b] Highly selected group.

TABLE 2

I. Q. AVERAGES BY GRADES

GRADES	NUMBER OF CASES	I. Q. AVERAGE
1st, 2nd, 3rd and 4th	882	75.9
5th and 6th	587	75.7
7th and 8th	325	85.9
9th, 10th, 11th and 12th	149	94.7

TABLE 3

I. Q. AVERAGES BY COUNTIES

COUNTY	NUMBER OF CASES	I. Q. AVERAGE	PER CENT OF COUNTY'S SCHOOL ENROLLMENT
K	847	83.8	42%
C	918	74.8	24%
H	180	76.1	

3. Interpretation of these tables and of other results. In examining table 1 the 5-6-year group, the 7-year group and the 15-year group reveal selective factors at work. Especially the first and last age groups have numbers that make them incomparable to the remaining age groups.

Also the 7-year group is a selected group and it is highly probable that if this group numbered from 180 to 190 subjects, like the subsequent groups,

the I. Q. average would be 82 or 83. But allowing environmental factors instead of selection to account for the entire difference between the 7- and 8-year old groups, then the extreme difference in I. Q. average as we ascend the chronological scale between any age groups is 12 points. The difference between the average of the 7-year group and the average for the entire group is about 6 I. Q. points. The difference between the average of the 7-year group and the average of an Urban community with the same *grade* distribution as the one in question would be about 16 I. Q. points. Thus giving environmental factors the most liberal terms that are possible, environment can only account for 37 per cent of the deficient of our subjects. It would probably be more nearly correct to state that environmental factors are responsible for about 25 per cent, and hereditary factors for 75 per cent of the subaverage mentality of our subjects, since (1) our subjects were somewhat super-representative of the counties investigated, (2) the 7-year age group was a selected group from this super-representative group.

This proposed interpretation of the causative elements involved in our I. Q. results is strengthened by an analysis of the 15 year-upward age group. The members of this group range from 15 to 23 years, more than three-quarters of whom were in grades 6 to 12. In table 1 we have seen that the I. Q. drops slowly from the 7- through the 14-year age group. In table 2 we note, nevertheless, that there is a 10 point rise in the combined 7th and 8th grade I. Q. average as compared to the 5th and 6th grades, and also as compared to the first 4 grades. This is stating that although the I. Q. decreases as we ascend the chronological scale up to 15 the I. Q. increases as we ascend from the lower 6 grades to the 7th and 8th grades. How are these seemingly conflicting statements to be interpreted and reconciled? The answer is to be discovered in the grade distribution of the 15 year-upward group. We find the 442 members of this group are distributed thus: 132 in the high school; 109 in grades 1–6; 201 in grades 7 and 8. That is, 201 of the 325 pupils in the 7th- and 8th-grade group are members of the 15 year-upward age group. Hence the 10 point I. Q. superiority of the 7th- and 8th-grade group over the lower grades is, in part, a consequence of the inclusion of 201 members of the 15 year-age group, and is in part a consequence of the presence of 124 selected 12, 13 and 14 year-old pupils.

Therefore, we must conclude that the slow decline of I. Q. in the age groups is for the most part due to environmental factors; but that the marked increase of the 7th and 8th grade I. Q. is *not* due to environmental factors (more and better education) but is a function of selection, operating on the basis of innate intelligence.

Little comment need be made regarding table 3. The 9.0 point I. Q. superiority of *K* county over *C* county, despite an economic, social, and

educational superiority of *C* county must be explained entirely on the basis of hereditary differences.

In one private school, founded and maintained by outsiders, correlations were made between chronological age and I. Q., and between chronological age and Educational Quotient on 257 pupils. A correlation of -0.23 ± 0.041 was discovered to exist between the former, and between chronological age and Educational Quotient the correlation was -0.1 ± 0.04. On 796 additional children the correlation between chronological age and I. Q. was -0.005 ± 0.026.

Two observations should be noted here. First, both correlations between chronological age and I. Q., although negative, are *small;* secondly, the correlation on the 796 children with poorer educational advantages more nearly approaches zero; that is, a better education seems to have accented the slight decline in I. Q. as we ascend the chronological scale.

* The writer wishes to gratefully acknowledge the financial aid he received for this experiment from the BACHE FUND.

[1] NATIONAL RESEARCH FELLOW.

CROSSING OVER IN THE THIRD LINKAGE GROUP IN OENOTHERA[1]

BY GEORGE H. SHULL

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Communicated November 19, 1926

Announcement was made last year[2] that a gene for double flowers (mut. *supplena*) in *Oenothera Lamarckiana* is closely linked with one of the genes for old-gold flower-color (mut. *vetaurea*), and that, since the latter factor is independent in its inheritance, from both of the previously known linkage groups,[3] the genes for doubleness and old-gold are the first discovered factors of linkage group III.

The evidence for the close linkage of these two genes was derived from a single F_2 family (24130) which was produced by self-fertilizing an F_1 diheterozygote, and which consisted of the two non-crossover classes, 94 yellow singles and 22 old-gold doubles, and no crossovers.

In order to determine how close the linkage is between these two genes, 31 of the dominant yellow singles in family 24130 were pollinated with the pollen of a single specimen of double-recessive old-gold double in the same family, and the F_3 families from these backcrosses have been grown during the past summer (1926). Of these 31 families, 10 consisted only of 1157 yellow-flowered singles, and 21 families split into yellow and old-gold and into singles and doubles, thus showing as close agreement as possible

with the expected 1:2 ratio of homozygotes and heterozygotes among the dominant individuals of the F_2 family 24130, and implying that the 4.3:1 ratio in that family owed its deviation from the typical 3:1 ratio to the differential elimination of a portion of the recessive group, without in any way modifying the composition of the dominant group.

This is quite a different result from that which would have been observable had old-gold and doubleness been included in linkage group I, for in that case all of the 31 families would probably have split, since at least one, and probably both, of the *Lamarckiana* lethals, l_1 and l_2, were present[2] in the F_2 plants, thus causing them to be heterozygous for all differential factors of linkage group I. One such differential factor, that for *rubricalyx* bud color, being a Mendelian dominant, was present in all plants of family 24130 although known to have been heterozygous in the F_1 parent of that family. That this factor was also really heterozygous in the plants of family 24130, though present in all of them, was demonstrated by two lines of evidence in the F_3 families: (*a*) An outcross of the *rubricalyx*-budded old-gold double-flowered pollen-parent of the 31 families here under consideration, to a green-hypanthium F_1 yellow single, produced (family 2588) 43 *rubricalyx*-budded plants and 63 green-hypanthium plants; and (*b*) this entire block of 31 F_3 families produced by sib-crosses in family 24130, together with family 2587, which was produced by a self-fertilization within the same family, consisted of 3010 *rubricalyx* and 5 *pervirens*, the latter being of the P_1 maternal type, which had no red pigmentation either on buds or stems. These 5 green individuals thus seemingly represent a crossing over of about 1.82 per cent between the factor for *rubricalyx* bud color and its accompanying lethal factor.

The 21 F_3 families which split with reference to flower color and doubleness included a total of 946 yellow singles, 810 old-gold doubles, and *one yellow double cross-over*. The moderate deficiency of the old-gold doubles in this group of families illustrates a condition which is often found and doubtless indicates a relative degree of physiological inadequacy of the old-gold double as compared with the yellow single type. The cross-over ratio shown in this group of families is very low, only 0.057 per cent, or slightly over one-twentieth of one per cent, but at any rate the results show that *old-gold and doubleness can be separated from each other.*

In addition to these F_3 families derived from the F_2 family No. 24130, I had 16 other families from as many different crosses between diheterozygous yellow singles and double-recessive old-gold doubles. Omitting one of these families (25122) because the simultaneous presence of the *brevistylis* character rendered the classification of some of the individuals doubtful, the remaining fifteen families consisted of a total of 411 yellow singles, 449 old-gold doubles, *6 yellow doubles and 2 old-gold singles*, thus showing a considerably higher incidence of crossing over than in the first

set of families presented above. The 8 cross-over individuals in a total of 868, is a cross-over percentage of 0.92 per cent. The highest percentage of crossing over in this group of families was shown in family 2588 in which there were two yellow doubles and one old-gold single in a total of 106 individuals, the non-cross-over classes consisting of 48 yellow singles and 55 old-gold doubles. The percentage of crossing over in this family is 2.83 per cent.

There were also 15 families in my cultures of the past season which were produced by self-fertilizing diheterozygous yellow singles. Three of these families (25115, 25119, 25121) must be omitted for the present because of doubts about the classification of plants simultaneously *brevistylis* and *supplena*. Of the remaining 12 families several were produced by self-fertilization of plants which were also heterozygous in sulfur-colored flowers, so that the non-cross-over class in these families consisted of a mixture of yellow singles and sulfur singles on the one hand, and of old-gold doubles on the other. These 12 families contained a total of *5 yellow doubles and 5 old-gold singles* to 767 yellow singles, 22 sulfur singles and 221 old-gold doubles. The linkage ratio 789:5:5:221 is a nearly perfect example of the self-fertilization ratio with the linked factors in the coupling phase, the only deviation being again a moderate deficiency in the number of the double-recessive class. Assuming that this deviation is due, as in family 24130, merely to differential elimination of a portion of the old-gold doubles, the ratio should be about 789:5:5:260, thus indicating a cross-over frequency of about 0.95 per cent.

The highest percentage of crossing over in this last group of families was seen in family 25136, which consisted of 79 yellow singles, 5 sulfur singles, 26 old-gold doubles and 2 old-gold singles, a percentage of crossing over of about 1.8 per cent.

The most significant feature of this demonstration that crossing over occurs in the third linkage group in Oenothera is the light it throws on the mechanism of crossing over in this group of plants. Gates[4] has argued that the cytological findings are not favorable to an interchange of factors between homologous chromosomes, and Cleland[5] has found an arrangement and behavior of the chromosomes during meiosis which suggest that linkage phenomena might be due to the end-to-end union of non-homologous chromosomes to form circles, and such a distribution of the component chromosomes of the circle that all the maternal members pass to one pole, the corresponding paternal chromosomes going to the other pole. Crossing over in this last case may be interpreted as due to irregularities in the distribution of the chromosomes of the circle, whereby one or more paternal chromosomes go to the otherwise maternal pole and *vice versa*.

The Oenothera forms used in this series of breedings have been utilized to a certain extent by Cleland in his cytological studies, but in no case has more than one circle of temporarily united chromosomes been found in

them, and it seems fair to assume, therefore, that only one linkage group can find an explanation based on the inclusion of non-homologous chromosomes in a circle. If there be such relationship between linkage and the arrangement of chromosomes into circles, it would seem most reasonable to identify the large number of known factors of linkage group I with the circle of united chromosomes; then each factor which is independent of linkage group I must be supposed to lie in one of the free pairs of chromosomes. Crossing over within the third linkage group means, therefore, that such crossing over consists in the *exchange of factors between the two chromosomes of the same pair*, in other words, it is here at any rate an intrazygous process, whatever may be the cytological details by which such exchange is brought about. Whether any of the linkage phenomena in Oenothera is synzygous in nature (produced by the cohesion of non-homologus chromosomes) remains to be demonstrated.

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[2] Shull, G. H., 1925, "The Third Linkage Group in Oenothera," *Proc. Nat. Acad. Sci.*, **11**, 715–718.

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GROUPS GENERATED BY TWO OPERATORS OF ORDER THREE WHOSE PRODUCT IS OF ORDER THREE

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It is well known that the group of movements of the regular tetrahedron is generated by two operators of order three whose product is also of this order but that these conditions do not determine this group. On the other hand, the group is completely determined by the fact that it can be generated by two operators of order three whose product is of order two. In the present article it will always be assumed that the operators under consideration are group operators and hence they obey the associative law of multiplication but not necessarily the commutative law when they are thus combined. The main object is to determine fundamental properties

of all the groups which can be generated by two operators of order three whose product is also of this order. It will appear that these groups constitute an elementary infinite system composed of groups whose orders are of the form $3n^2$, and of quotient groups thereof, where n may have any integral value. In the special case when $n = 2$ we have the tetrahedral group noted above, and hence the present paper has close contact with the groups of the regular solids.

In what follows it will be assumed that S_1, S_2 represent two operators which satisfy the following conditions:

$$S_1^3 = S_2^3 = (S_1S_2)^3 = 1$$

and that none of the three operators S_1, S_2, S_1S_2 is the identity. We shall represent the order of $S_1S_2^2$ by n, and consider the conjugates of $S_1S_2^2$ under S_1 and S_2. These conjugates may be represented as follows:

$$S_1S_2^2 \quad S_2^2S_1 \quad S_1^2S_2^2S_1^2 = S_2S_1S_2.$$

Moreover, these conjugates are commutative and each of them is the inverse of the product of the other two. The order of the abelian group generated by $S_1S_2^2$ and $S_2^2S_1$ cannot exceed n^2 and as this abelian group is invariant under S_1 and S_2 these two operators generate a group whose order cannot exceed $3n^2$. Hence it remains only to prove that for every integral value of n there is a group of order $3n^2$ which is generated by two operators which satisfy the conditions imposed on S_1 and S_2.

Suppose first that n is of the form p^m, where p is any prime number except 3, and consider the abelian group H of order p^{2m}, whose invariants are p^m, p^m. Two independent generators of this abelian group will be denoted by t_1 and t_2. It is easy to verify that H may be made isomorphic with itself by letting t_2 correspond to t_1 and $t_1^{-1}t_2^{-1}$ correspond to t_2, and that this automorphism is of period 3. Moreover, only the identity corresponds to itself in this automorphism since the multipliers corresponding to this automorphism generate a group of order p^{2m}. If we represent by S_1 the operator of order 3 in the group of isomorphisms of H which effects this automorphism it results that the group G generated by H and S_1 involves only operators of order 3 in addition to the operators in H, and that all the p^{2m} subgroups of order 3 contained in G are conjugate under H. Hence we can select S_2 from the operators of the co-set to which S_1 belongs with respect to H so that both S_2 and S_1S_2 are of order 3 while $S_1S_2^2 = t_1$. The group G is obviously generated by S_1 and S_2.

In the excepted case when $p = 3$ the situation is somewhat different since a group of order 3^{2m+1} must involve at least 3 invariant operators, and hence at least three of the operators of H must correspond to themselves in this case. The group of order $3p^{2m}$ considered in the preceding paragraph involves no invariant operator besides the identity. In the present

case S_1 may be supposed to effect the automorphism in which t_1 corresponds to $t_2^3 t_1$ while t_2 corresponds to $t_1^{-1} t_1^{-2}$. As the commutators corresponding to this automorphism generate a group of order 3^{2m-1} exactly three of the operators of H correspond to themselves when H is transformed by S_1. Since both of the products $S_1 t_1^{\alpha}$, $S_1 t_2^{\alpha}$ are of order 3 irrespective of the value of α it results that all the operators of G besides those contained in H are again of order 3, and hence the number of operators of order 3 in G is now two-thirds of the order of G increased by 8, while in the preceding case the number of these operators was equal to two-thirds of the order of G. Moreover, in the present case there are four sets of conjugate subgroups of order 3, besides the invariant subgroup of this order. Three of these sets are separately composed of 3^{2m-1} such subgroups while the fourth involves 4 such subgroups.

When n is not a power of a prime, H is the direct product of its Sylow subgroups since it is abelian. All the products obtained by multiplying the operators of H by S_1 are, therefore, again of order 3. When n is prime to 3 the n^2 subgroups of order 3 contained in G constitute a single set of conjugates under H, while G involves four sets of conjugate subgroups of order 3, besides the invariant subgroup of this order, whenever n is divisible by 3. Each of three sets is composed of $n^2/3$ such subgroups while the remaining set involves only four such subgroups just as in the case when n is a power of 3. Hence we have established the following theorem: *Two operators of order 3 whose product is also of this order but which are not otherwise restricted generate a group of infinite order. The product of one of these operators into the square of the other may have an arbitrary order n, and if this order is given but no additional condition is imposed on these two operators then they generate a group of order $3n^2$ in which two-thirds of the operators are of order 3 when n is prime to 3, and 8 more operators are of this order when n is divisible by 3. In all cases when $n > 1$ the group contains an abelian invariant subgroup generated by two independent operators of the same order.* It may be added that when $n = 2$ the condition that $S_1 S_2$ is of order 3 becomes redundant but this is not true when $n > 2$.

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